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**Abstract** The effect of polyethylene glycol (PEG) having molecular weight of 400 and 600 on stability of shellac waxfree prepared by solvent-evaporation method was reported in the present paper. The stability of shellac was tested by life under heat at 125 $^{o}$C for 10 , 30 , 90 , and 180 minutes. It was found that that stability of shellac decreased with heating time at 125 $^{o}$C. PEG400 gave the most stable effect of shellac for 30 minutes of heating, whereas at 90 minutes and above PEG600 gave the most effect of shellac stability as shown by insoluble solid test and FTIR. The WVTR showed that water vapour barrier properties of PEG600/shellac was beter than that of PEG400/shellac system.

## 1. Introduction

Shellac is a natural polymer secreated by lac insects cultivated in host tree in tropical countries such as India, Thailand and Indonesia, which has been used in food, cosmetic, and pharmaceutical industry [1] .It is a complex mixture of single esters and polyesters containing hydroxyl and carboxyl [2] It is insoluble in water but solublene in alcohol and alkali solution [3]. The application of shellac gradually decreased due to its stability, solubility, and the substitution of semisynthetcs and synthentic polymer. Several efforts have been done to solve these issue including modification into salt formation [4], and shellac derivative [5]. Natural polymer also tended to be brittle, and adding plasticizer may improve the flexibility of polymer by reducing the intermolecular forces, soften the rigidity of the film structure and increase mobility of biopolymer chains, thus affecting mechanical properties such as decreasing tensile strength and increasing percent elongation [6]. Plasticizer castor oil and dibutyl phthalate reduced water favor permeability but Polyethylene glycol (PEG) increased water vapor permeability of hydroxypropyl methylcellulose (HPMC), while in othes case palsticizer did not change the water favor permeability [7] suggesting that the solubility and the affinity of plasticizer to the polymer. Molecular weight of PEG play important role in stability of shellac [8,9]. In our previous studies [8], it showed that PEG1000 gave better effect on shellac stability compared to that of PEG2000. Therefore, the aim of the present study to extend the effect of molecular weight of PEG by using PEG 400 and PEG600. The stability was tested by heating shellac for different times.

## 2. Experimental

### *2.1 Sample preparation*

The shellac type was wax free supplied by Sigma Aldrich UK. Alcohol 96 % was supplied by Merck Germany. Plasticizer polyethylene glycol was supplied by Sigma Aldrich UK. All films presented were prepared by solution-casting. Shellac films were made by dissolving 1.25 gr of shellac in 12.5 ml ethanol (96%), while PEG/shellac films (10 wt%) were prepared by mixing and stirring shellac solution and PEG solution. The solution was then cast into Petri dish, then dried at 50 °C for 7 hours before being analyzed.

### *2.2. Characterization*

#### *2.2.1. Insoluble solid test*

Insoluble solid test is one of the method to quantify polymerization of shellac due to heating or moisture. In this studies, the polymerization was accelerated by heating at 125°C for 10, 30, 90, 180 and 360 minutes. The heated shellac film was dissolved in ethanol (96%) for 3 hours. The solution was then filtered using a metal filter (150 mesh). The insoluble solid was dried at room temperature until a constant weight was obtained and the percentage was calculated.

#### *2.2.2. Fourier Transform Infra Red (FTIR)*

FTIR was used to clarify the result of insoluble solid test by monitoring the peak intensities of O-H and C=O group. The intrument was a Thermo Nicolet NEXUS spectrometer along with a MCT (mercury cadmium telluride) detector cooled by liquid nitrogen. The wavelength of interest ranges from 700 to 4000 $cm^{-1}$ and was collected with resolution of 4 $cm^{-1}$ and 64 scans. Omnic software was used to collect and analyse the spectra.

#### *2.2.3. Thermogravimetry analyzer (TGA)*

Mettler Toledo TG50 Thermogravimetric with analyser using an alumina crucible was used in TGA measurements at a heating rate of 20 $^{\circ}$C/min between 35 and 800 $^{\circ}$C after an initial isothermal stage where the sample was kept at 35 $^{\circ}$C for 15 minutes. The analysis was performed under a nitrogen atmosphere with a flow rate of 10 ml/min.

#### *2.2.4. Water vapour transmission rate (WVTR).*

The water vapor transmission rate (WVTR) which represent the barrier water properties of shellac and plasticized shellac was measured using Payne cups supplied by Sheen Instruments. The cups had an exposed surface area of 10 $cm^2$ and contained silica gel desiccant (8 g in each cup), which was closed by the material to be tested and dried overnight in an oven at 100 °C. They were placed in a controlled atmosphere (humidity chamber) and were weighed at suitable time intervals. The WVTR result was calculated from the following formula [10]:

$$WVTR = (240 \times m) / (S \times t) \quad (1)$$

where t is the total duration in hours, m is the increase in mass in milligrams of the assembly during the time t, and S is surface area exposed by the Payne cups. The WVTR was measured in tropical packaging standar, i,e, 23 $^{\circ}$C and 85 %,. The relative humidities of 85% were achieved by placing saturated potassium chloride salt solutions, in a humidity chamber [11]. Shellac and PEG/shellac films were equilibrated in the humidity oven at 23 $^{\circ}$C and 85 % relative humidity (RH) for 24 hours before performing the WVTR measurement.

## 3. Results and Discussions

Stability of shellac due to polymerization among hydroxyl and carboxyl groups [12] causing the change of properties such as water vapor barrier properties , glass transition temparature, acid value, and mechanical properties. Therefore, some of these properties are investigated in this report. From our previous studies [8], the stability of shellac could be improved when incoporating with PEG1000

and PEG2000, to verify further effect of molecular weight, PEG400 and PEG600 is used in this studies.

The insoluble solid is a direct consequence of shellac polymerization due increased amount of hard resin composed of polyster (Limmatpavirat,2004). Figure 1 shows the insoluble solid of shellac, PEG400-shellac (10 wt/wt %), and PEG600-shellac (10 wt/wt %) as a function time heated at 125 $^{o}$C. It shows that the insoluble solid is presence not only in native shellac but also in plasticized shellac indicating that PEG could not stop polymerization. The level of polymerization increases significantly after heating for 90 minutes and more. The amount of insoluble solid in both plasticized shellacs is lower that those of native shellac indicating that PEG400 and PEG600 slow down polymerization. Heating time shows different effect of insoluble solid of plasticized shellac. Heating time for 30 minutes and less, the insoluble solid of PEG400-shellac system is lower than that of PEG600-shellac system, whereas heating for 90 minutes and above the insoluble solid of PEG600-shellac system is lower than that of PEG400-shellac system. Mobility of PEG chains in shellac matrix may affect how PEG interacts with shellac. For long heating time, less mobility of PEG600 can keep its interaction with shellac while high mobility of PEG400 distisburbs its contact with shellac resulting less effect of slowing down of shellac polymerization. Our previous studies showed that the trend of insoluble solid in PEG1000-shellac (10 wt/wt %) was lower than that of PEG2000-shellac (10 wt/wt %), and not affected by heating time supporting our present results.

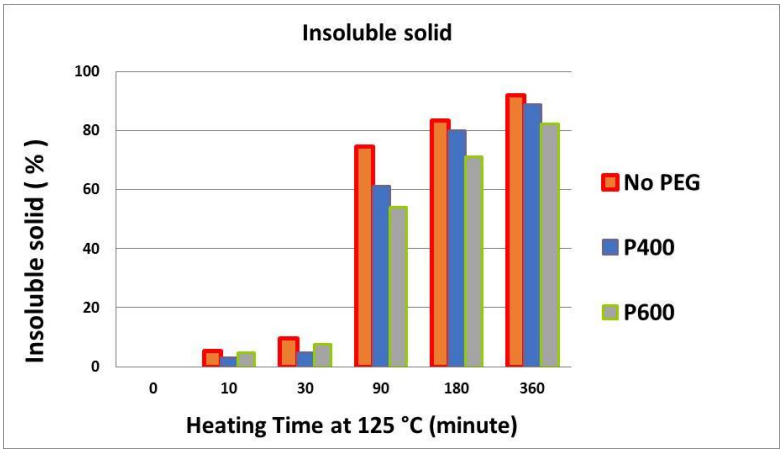



**Figure 1.** Insoluble solid of shellac, PEG400-shellac, and PEG600-shellac system as a function of time heated at 125 $^{o}$C

Figure 2 and 3 show the FTIR spectra of PEG400-shellac (10 wt/wt %) and PEG600-shellac (10 wt/wt %) heated at different time at 125 $^{\circ}$C (data of native shellac is presented here). There are main peaks that may be affected by polymerization of shellac according to polymerimization mechanisms proposed by Limmatpavirat,*et.al* [13], i.e., O-H group at 3400 cm$^{-1}$ and C=O at 1730 cm$^{-1}$. Polymerization will be assigned by the decrease of O-H group, and by the increase of C=O group presence in the samples. General trend in both samples show that the peak intensity of O-H decreases but C=O increases with increasing heating time as shown in Figure 4a and b. The peak intensity of O-H in both PEG400-shellac and PEG600-shellac are higher than that of native shellac (Figure 4a), while opposite trend is observed at peak intensity of C=O group (Figure 4b). The peak intensity of O-H group in PEG600-shellac is higher than that of PEG400-shellac, while opposite trend of C=O group peak intensity is observed when samples are heated for 90 minutes and above. The results support the result of insoluble solid (Figure 1).

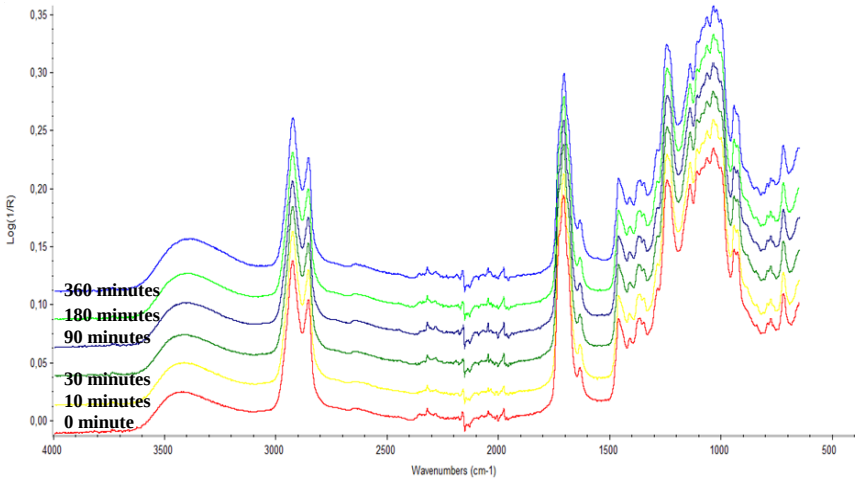



**Figure 2**. FTIR spectral o Shellac/ PEG400 heated 125 $^{o}$ with variation of heating time

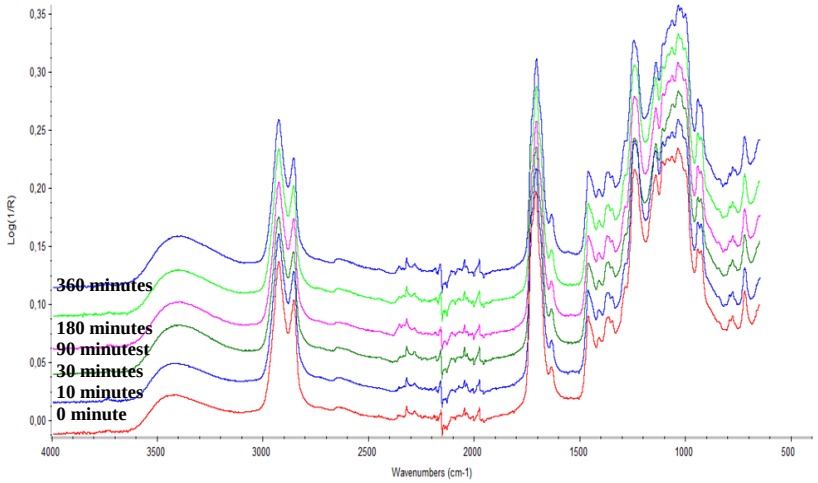
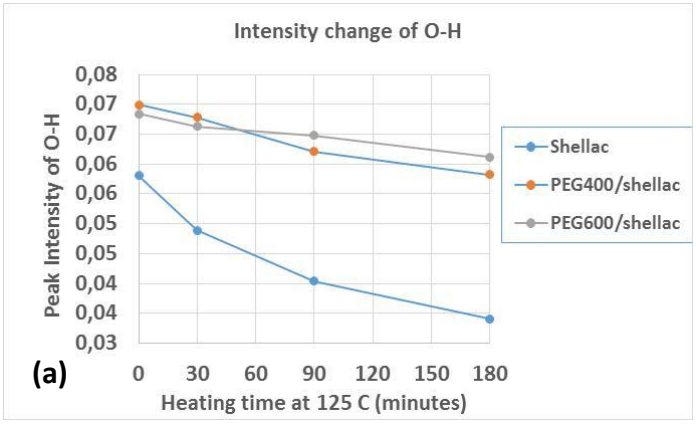



**Figure 3.** FTIR spectral o Shellac/ PEG600 heated 125 $^{o}$ with variation of heating time



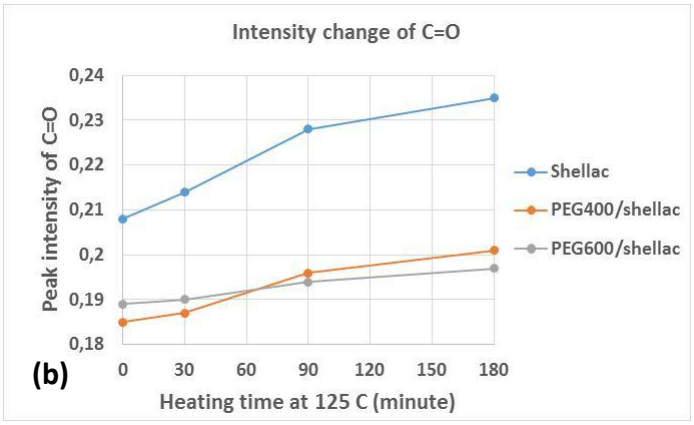



**Figure 4.** Peak intensity as a funtction heating time at 125 $^{o}$C of a). O-H, b). C=O group

Thermal stability of samples when they are heated can be given by Thermogravimetric Analysis (TGA). It measures measure the weight change of sample due to the formation of volatile products in relation to change in temperature. Thermogram of shellac, PEG400, and PEG400-shellac is shown in Figure 5, while thermogram of shellac, PEG600, and PEG600-shellac is shown in Figure 6. There are 3 areas of weight loss in all samples,i.e, first: in the range 35-150 $^{\circ}$C, second: in the range 250 – 475$^{\circ}$C, and third: above 500$^{\circ}$C. Each weight lost relates to water or solvent present in the sample, structural decomposition of the shellac, and remained compound or carbon, respectively. No significant different in water/solvent content was observed for all samples. Degradation temperature of PEG-shellac (second weight lost) is higher that those of either PEG or shellac indicating that PEG improved thermal stability of shellac, and vice versa. The weight lost in the range 250 – 475$^{\circ}$C of PEG600-shellac was 92,94 wt%, whereas 95,12 wt% for PEG400-shellac.

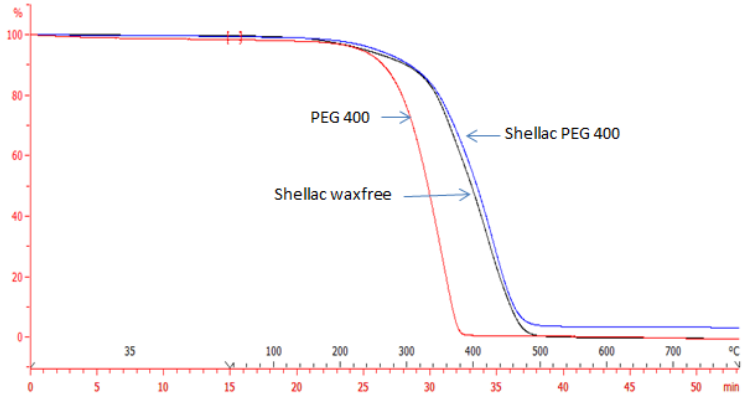



**Figure 5**. Thermogram of shellac, PEG400, and PEG400-shellac

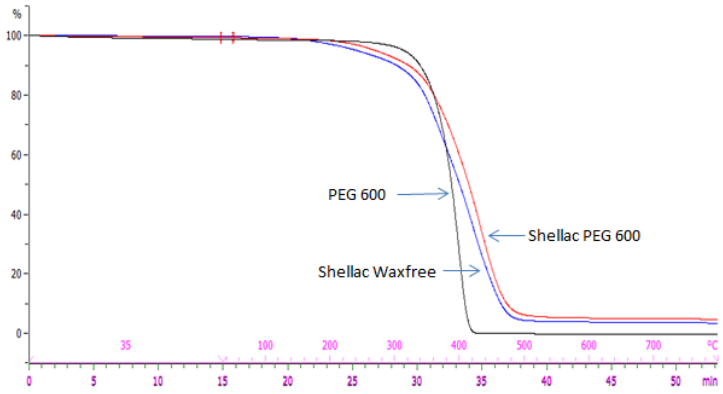



**Figure 6**. Thermogram of shellac, PEG600, and PEG600-shellac

Water vapor transmission rate (WVTR) of shellac and plasticized shellac is given in Figure 7, which shows that adding either PEG400 or PEG600 reduces water barrier properties of shellac. PEG disturbs the intra molecular bonds of shellac resulting in the reduction of shellac chain packing, in addition to hydrophylic properties of shellac. Similar effect of PEG to polymer was reported by other studies [14,15] PEG600 gave better water barrier properties to shellac compared to given by PEG400. As the WVTR was measured for flms with heating treatment, higher content of hard resin in PEG600-shellac may relate to its water barrier properties.

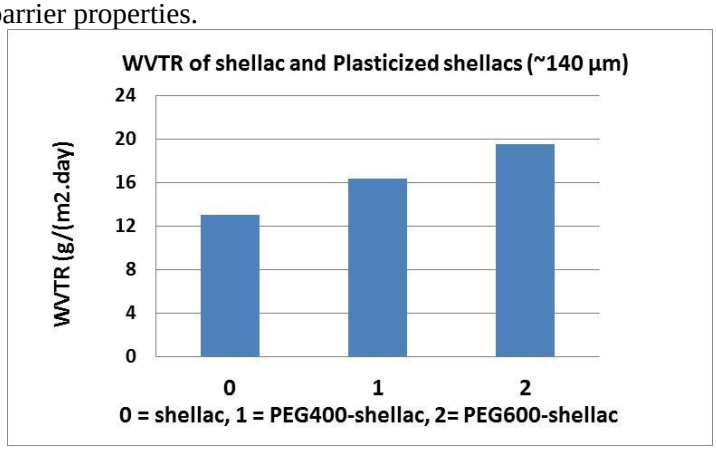



**Figure 7**. Water vapor transmission rate of shellacm PEG400-shellac, and PEG600-shellac

## 4. Conclusion

It has been shown that heating of shellac and plasticized shellac at 125 $^{o}$C caused polymerization, and the level of it increased with increasing heating time. PEG slowed down shellac polymerization, which was affected by molecular weight of PEG. The molecular weight affected the thermal degradation, and the water barrier properties.

### Acknowledgement

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